

Modeling the AA2024/CFRP Galvanic Couple Under a Dynamic Electrolyte Drop

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ABSTRACT

The galvanic interactions between AA2024 and Carbon Fiber Reinforced Polymer under a dynamic drop of NaCl electrolyte were studied. The use of a dynamic electrolyte provided the unique opportunity to investigate both thick and ultra-thin electrolyte systems. A modeling approach was achieved by solving the Nernst-Planck equations in a 2D dynamic domain. Two kinds of boundary conditions were considered: electrochemical and physicochemical. Huge differences were found in the galvanic corrosion process at the beginning of the droplet evaporation (initial height 1.8 mm) and after 24 h of a continuum evaporation process at 25 °C and 85% RH (final size 0.06 mm).

Key words: Modeling, Droplet, Dynamic Electrolytes, AA2024.

INTRODUCTION

The gap between fully immersed and ultra-thin film electrochemical measurements is wide, which suggests that the two conditions are independent of one another. There is a lot of work describing experiments, results, and trends regarding completely immersed electrochemical tests. However, in corrosion tests under thin electrolyte films, the information is not so abundant. A classical three-electrode cell used in conventional electrochemical tests cannot easily be scaled for immersion in electrolytes of micron thickness. In fields such as atmospheric corrosion, for example, the thickness of

the electrolyte could go from a few micrometers up to millimeters depending on the condensation-evaporation process.

The above justifies that modeling has recently become an essential tool for electrochemical predictions in such applications as several works have proved it.¹⁻¹⁰ However, few works have been published to avoid oversimplification in models dealing with atmospheric corrosion problems that account for dynamic electrolytes under evaporation and condensation phenomena.^{3,6} The number decreases even more if the research also includes homogeneous chemical reactions and migration effects. Regarding the works of Montoya et al., they have been able to predict and validate the propagation of acidic and alkaline fronts by using both thick and thin chemically modified gel-electrolyte films during the galvanic corrosion phenomenon of different couples.^{8,9,11} However, it has always been achieved considering a static electrolyte.

Recently an exciting review has been published regarding modeling corrosion under droplet electrolytes.¹² After studying and discussing several analytic and numerical models, they conclude that the influence of the geometric droplet evolution on corrosion mechanisms should still be modeled.

It is the purpose of this work to continue bridging the gap among experimental findings and modeling results in the atmospheric corrosion field. A transport model (solving the Nernst-Planck equations) was developed to study the electrochemical interactions between the couple AA2024 and CFRP under a standard dynamic drop of electrolyte (originally NaCl 0.06M). The temperature was set as 25°C for 24 h. The RH remained at 85% during simulations.

MODELING

To predict the electrochemical interactions in a dynamic electrolyte droplet on top of the galvanic couple AA2024/CFRP, two different mathematical models were solved simultaneously by Finite Element Method: the transient concentration of eleven different chemical species (Nernst Planck equations), and the corresponding geometrical considerations involved in a dynamic ellipsoid (subjected to condensation/evaporation boundary conditions).

Nernst-Planck Equations

A transport model using the Nernst-Planck equations was built to find transient information about the galvanic system's potential, current, and chemical species distributions under an electrolyte drop.^{13,14} These equations were solved using the Finite Element Method in a homemade computational code written in Python. The governing equation was Equation 1:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + R_i \quad (1)$$

where C_i , R_i , and N_i are the concentration (mol/m³), the net generation/consumption rate due to chemical reactions (mol/m³ s), and the molar flux (mol/m² s), respectively, of species i . Neglecting the convective term, and considering a dilute solution, the flux is expressed according to Equation 2:

$$N_i = -D_i \nabla C_i - z_i u_i F C_i \nabla \varphi \quad (2)$$

where D_i , z_i and u_i are the diffusion coefficient (m²/s), the charge number, and the ionic mobility, respectively, (s mol/kg) of species i ; φ is the electric potential within the electrolyte (V) and F is the Faraday constant (96485 C/mol). u_i can be estimated through the Nernst-Einstein equation (Eq. 3):

$$u_i = \frac{-D_i}{RT} \quad (3)$$

where T is the absolute temperature (K) and R is the universal gas constant (8314 J/mol K). The combination of Equations 1 and 2 results in the well-known Nernst-Planck equation (Eq. 4).

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + z_i u_i F \nabla (C_i \nabla \phi) + R_i, \quad (4)$$

If the number of chemical species considered is n , then the number of unknowns in the system is $n + 1$ due to ϕ . The extra-equation for solving the global system is the electroneutrality condition (Eq. 5).

$$0 = \sum z_i C_i, \quad (5)$$

Figure 1 is the schematic representation of the studied system. The domain where the above equations were solved was a drop of electrolyte with an initial radius of 1.8 mm that was deposited on top of the surface of two different conductive materials. As the boundary condition on the electrolyte border Γ_3 , was not in contact with the conductive surface, a nil flux of species and current was considered. Two kinds of boundary conditions were used regarding the active electrochemical boundaries Γ_1 and Γ_2 (bottom part of the electrolyte). The first one is for the O_2 reduction and the latter for the Al oxidation. Both of them were written as Equations. 6 and 7, respectively:

$$J_{O_2} = -knFC_{O_2} e^{\left\{ \frac{(1-\alpha)nF(V-\phi)}{RT} \right\}} \quad (6)$$

$$J_{Al^{3+}} = knFe^{\left\{ \frac{\alpha nF(V-\phi)}{RT} \right\}} \quad (7)$$

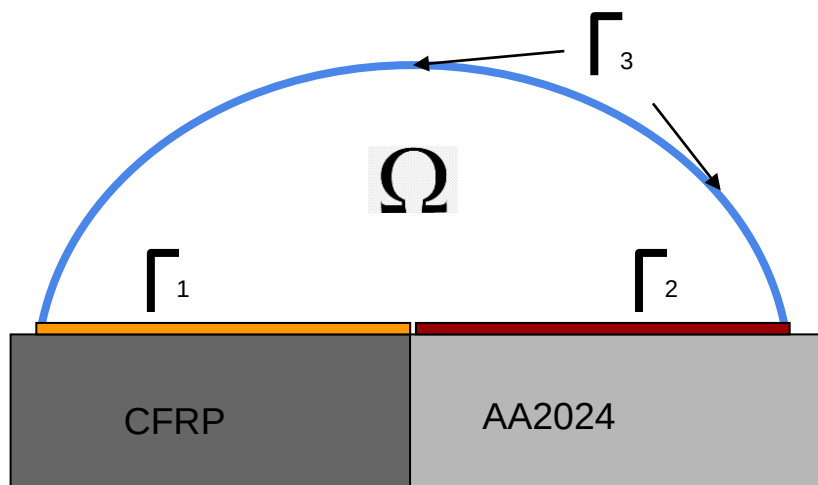


Figure 1: Schematic figure of the simulated system, considering three different boundaries (Γ_1 , Γ_2 , and Γ_3) and one dynamic domain Ω .

Additionally, the dissolved oxygen concentration on the electrolyte/air boundary (Γ_3) was considered as $0.26 \text{ (mol/m}^3\text{)}$.²¹ Regarding R_i , in Equation 4, just six homogeneous chemical reactions were used for the sake of simplicity and are presented in Table 1. On the other hand, two electrochemical reactions were taken into account (Eqs. 8 and 9):

Al oxidation for AA2024:



And oxygen (on the CRFP surface) reduction:

